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Raman Spectra of some Organic Sulphides, Part I.

By

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(*Received for publication, 1st May, 1931.*)

ABSTRACT

The paper describes the results of investigation of the Raman spectra of methyl, ethyl, propyl, butyl, isobutyl, and allyl sulphides and methyl and ethyl disulphides. Methyl sulphide belongs to a triangular model AX_2 and the oscillations of this system are discussed on dynamical considerations. The C–S linkage is associated with two frequencies, a sharp intense one at about 691 and a diffuse one at 746, which are not appreciably affected by changes in the nature of the group attached to the carbon atom or by the difference in the chemical bond between the sulphur and carbon atoms. The disulphides show a prominent new line at 512 which presumably represents the S–S oscillation. This value which is distinctly lower than for ν obtained from fluorescence and absorption bands for sulphur vapour points to the difference in the nature of the chemical bond between the sulphur atoms in S_2 and in the disulphides. A characteristic feature of C–S and S–S oscillations, revealed for the first time, is their peculiar tendency to split into components in ethyl and higher members of the series. A slight shift in the C–S oscillation of methyl sulphide is noticed in the disulphide. Allyl sulphide shows a prominent line at 1634 which is characteristic of ethylenic linkage. Differences in the character of the C–H band in the normal and corresponding iso-compounds are pointed out.

The Raman spectra of a number of organic sulphides * and disulphides have recently been investigated by the author

* Since this paper was under preparation, a note by V. N. Thatte and A. S. Ganesan describing the Raman frequencies of ethyl and allyl sulphides has appeared in Nature, 306, Feb. 28, 1931.

and the results are given in this paper. Of the liquids reported, methyl sulphide, methyl disulphide, and ethyl disulphide were obtained from the Palit Chemical Laboratory on loan through the kindness of Sir P. C. Ray. These were carefully fractionated and finally distilled in vacuum. The remaining liquids were all obtained from Messrs. Scherring Kahlbaum and were purified by distillation in vacuum. The spectrograms were taken with a glass high dispersion Fuess instrument using backed golden isozenith plates. The usual experimental arrangements were followed, the mercury arc being used for illumination. A comparison spectrum with iron arc was taken in all cases.

Results.

In Tables I to VIII the results of analysis of the Raman spectra of the sulphides and disulphides are given. The intensities of the Raman lines, their wave-lengths and the shifts in wave numbers are given under the various columns. The exciting lines λ 3650·1, 3654·8, 3663·3, 4046·6 4077·8, 4339·2, 4347·5 and 4358·3 are represented by the letters *a*, *b*, *c*, *d*, *e*, *f*, *g*, and *h* respectively. The following abbreviations regarding the nature of the lines are used. *S*—sharp, *d*—diffuse, *b*—broad, *dr*—diffuse towards the red, *dv*—diffuse towards the violet.

Discussion of Results.—Methyl sulphide being the simplest of the organic sulphides its Raman spectrum may first be considered. The liquid shows eight frequencies of which those at 1424, 2844, 2916 and 2984 are known to be definitely arising from the CH oscillations. Of the remaining four frequencies $\Delta\nu$ 284 and 1334 are weak and diffuse. $\Delta\nu$ 691 is the most intense and sharp and is accompanied by a diffuse and less intense component at $\Delta\nu$ 743 both of which presumably represent the same oscillation. The existence of these three distinct oscillations which are characteristic of the CSC group

TABLE I

Methyl Sulphide.

Intensity	λ_{Ra} A.U.	ν (Vac)	$\Delta\nu$	Intensity	λ_{Ra} A.U.	ν (vac)	$\Delta\nu$
3	4083·7	24480	$a-2909$	6 S	4493·8	22247	$h-691$
3	4089·8	24444	$b-2910$	2 d	4503·7	22197	$h-741$
0	4093·7	24421	$d-284$	0 dr	4573·0	21861	$d-2844$
3	4096·5	24404	$a-2985$	8	4587·4	21793	$d-2912$
1	4101·6	24374	$c-2916$	4 dv	4602·6	21721	$d-2984$
0	4113·0	24306	$c-2984$	1	4627·6	21603	$h-1335$ } $e-2913$ }
6 S	4163·8	24013	$d-692$				
2 d	4172·5	23960	$d-745$				
0	4277·7	23370	$d-1335$	1 rd	4647·0	21513	$h-1425$
0 vd	4294·0	23282	$d-1423$	2	4993·5	20020	$h-2918$
1 vd	4413·0	22654	$h-284$	0 d	5009·1	19958	$h-2980$

$\Delta\nu$	284	691	743	1335	1424	2841	2912	2984
	(1 vd)	(6 S)	(2 d)	(o d)	(1 vd)	(o d)	(8)	(4 d)
	35·2	14·47	13·46	7·49	7·02	3·516	3·433	3·351

$\Delta\nu$ 2844 and 2984 present structures which are symmetrical about the central strong line.

TABLE II

Methyl Disulphide.

Intensity	λ_{Ra} A.U.	ν (Vac)	$\Delta\nu$	Intensity	λ_{Ra} A.U.	ν (Vac)	$\Delta\nu$
3	4132·3	24193	$d-512$	0	4503·2	22200	$k-738$
3	4163·9	24009	$d-696$	6	4587·8	21791	$d-2914$
0 d	4172·0	23963	$d-742$	3 d	4603·1	21718	$d-2987$
0	4263·0	23451	$h+513$				$e-2915$ }
1 vd	4405·0	22695	$h-243$	0	4628·0	21601	$h-1337$ }
0 d	4413·0	22651	$h-284$	0	4647·0	21513	$h-1425$
6 S	4457·8	22426	$h-512$	3	4992·3	20025	$h-2913$
6 S	4494·6	22243	$h-695$	1 d	5010·0	19954	$h-2984$

$\Delta\nu$:—	243	284	512	695	740	1337	1425	2914	2987
	(1 vd)	(0 d)	(6 S)	(6 S)	(0 d)	(0)	(0 d)	(6)	(3 d)
μ :—	41·2	35·2	19·5	14·39	13·51	7·48	7·02	3·432	3·348

may be explained on the basis of dynamical considerations. As a first approximation the CH_3 group may be taken as one unit (X) and the structure represented by A X_2. Such a system may be expected to give three independent vibrational frequencies. The following table contains some of the physical constants of methyl and ethyl sulphides which are of interest here :—

	Electric moment [1] $\times 10^{-18}$.	Dielectric constant [2] (liquid).	Depolarisation value [3] of transversely scattered light. r % (liquid).	Magnetic birefringence Nitre [4] benzene = 100 (liquid).
Methyl sulphide	1·27	6·2	12·9	
Ethyl sulphide	...	7·2	18·2	−·08

The existence of an electric moment indicates definitely that in the molecule of methyl sulphide the methyl groups are not in the same line with the sulphur atom.

Of the three Raman frequencies which characterise the CSC group we may reasonably state that the most intense one at $\Delta\nu$ 691 and its component $\Delta\nu$ 743 correspond to a more or less symmetric oscillation of the molecule. In this mode of oscillation the sulphur atom vibrates along the axis of symmetry, the two CH_3 groups maintaining symmetry about this axis. $\Delta\nu$ 1335 may be ascribed to the transverse oscillation where the sulphur atom vibrates in the plane of the triangle along a line perpendicular to the symmetry axis, the distance between the CH_3 groups remaining unchanged. It is evident that the molecular force between the two X atoms should not affect this mode of oscillation. That it is so is seen from the fact that this frequency remains more or less constant in all the sulphides, the effect of lengthening the alkyl chain being inappreciable. The third frequency, *viz.*,

[1] Landolt, Bornstein Tabellen.
[2] ,, ,, ,,
[3] K. S. Krishnan, Phil. Mag., 50, p. 697, 1925.
[4] M. Ramanadhan, Ind. Journ. Phys., Vol. IV, p. 15, 1929.

TABLE III

Ethyl Sulphide.

Intensity.	λ_{Ra} A.U.	ν (Vac).	$\Delta\nu$	Intensity.	λ_{Ra} A.U.	ν (Vac).	$\Delta\nu$.
3	4087·5	24458	*a*—2931	3	4483·5	22298	*h*— 640
3 *b*	4094·1	24419	*a*—2970	3	4486·9	22281	*h*— 657
			b—2935	3	4493·9	22247	*h*— 691
0	4099·2	24388	*b*—2966	0 *vd*	4514·2	22146	*h*— 792
2	4103·1	24365	*c*—2925	2 *b*	4551·6	21964	*h*— 974
			d— 340	0	4561·2	21918	*h*—1020
2	4153·7	24068	*d*— 637	1	4567·3	21889	*h*—1049
2	4157·0	24049	*d*— 656	3	4580·3	21827	*d*—2878
2	4162·8	24016	*d*— 689	8	4591·1	21775	*d*—2930
0	4213·4	23727	*d*— 978	5 *b*	4597·9	21743	*d*—2962
0	4221·0	23684	*d*—1021	0 *vd*	4615·0	21662	*h*—1276
0	4226·0	23656	*d*—1049	2 *d*	4631·4	21586	*e*—2930
0	4229·0	23640	*d*—1065	1 *d*	4640·0	21546	*e*—2970
0 *vb*	4267·0	23429	*d*—1276	1 *d*	4647·0	21513	*h*—1425
0	4295·8	23272	*d*—1428	3 *d*	4653·4	21484	*h*—1454
1 *vb*	4300·6	23246	*d*—1459	2	4983·4	20061	*h*—2877

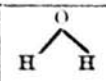
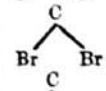
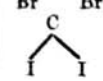
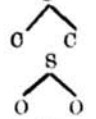
TABLE III—*contd.*

Intensity.	λ_{Ra} A.U.	ν (Vac).	$\Delta\nu$	Intensity.	λ_{Ra} A.U.	ν (Vac).	$\Delta\nu$
0	4416·5	22636	*h*— 302	4	4995·4	20013	*h*—2925
0	4423·1	22602	*h*— 336	2	5006·3	19969	*h*—2969
0	4434·0	22547	*h*— 391				

$\Delta\nu$	302	336	391	639	657	690	792	976	1020	1049	1065	1276	1426	1456	2878	2930	2966
	(0)	(0)	(0)	(3)	(3)	(3)	(*od*)	(2*b*)	(0)	(0)	(0)	(*od*)	(1 *d*)	(3 *d*)	(3)	(8)	(5*b*)
μ	33·3	29·8	25·6	15·6	15·22	14·49	12·63	10·25	9·80	9·53	9·39	7·27	7·01	6·87	3·475	3·413	3·371

$\Delta\nu$ 284 probably corresponds to the third mode of oscillation where the sulphur atom goes outward vibrating along the line of symmetry, while the CH_3 groups move in towards each other.

A comparison of the frequencies characteristic of the AX_2 systems both linear and non-linear reveal certain interesting features. The results obtained with all the AX_2 systems investigated so far are tabulated below.

	Substance *				
1	Water		—	3453	—
2	Nitrous oxide	N—O—N	—	1283	2226
3	Carbon dioxide	O—C—O	—	1388	—
4	Methylene chloride		283	697	734
5	Methylene bromide		178	578	634
6	Methylene iodide		119	487	573
7	Carbon disulphide	S—C—S	—	655,800	—
8	Propane		870	940	1050
9	Hydrogen sulphide		—	2572	—
10	Methyl sulphide		284	691,743	1335
11	Sulphur dioxide		526	1146	1340
12	Zinc methyl		506	617	1165

Most of them show three distinct Raman frequencies, of which the central one is usually very intense and sharp while the first and third are diffuse and much less intense.

* Data collected from several authors. References to the papers may be obtained from "The Raman effect, its significance for physics and chemistry" by S. Bhagavantam, Ind. Jour. Phys., Vol. V, p. 287, 1930.

TABLE IV

Ethyl Disulphide.

Intensity.	λ_{Ra} A.U.	ν (Vac).	$\Delta\nu$.	Intensity.	λ_{Ra} A.U.	ν (Vac).	$\Delta\nu$
3	4131·9	24195	*d*— 510	0	4432·6	22554	*h*— 384
1	4134·5	24180	*d*— 525	6	4457·2	22429	*h*— 509
4	4154·6	24063	*d*— 642	3	4460·4	22413	*h*— 525
1	4158·5	24040	*d*— 665	8	4483·5	22298	*h*— 640
0	4168·6	23986	*e*— 530	4	4489·1	22270	*h*— 668
0	4175·4	23943	*d*— 762	0 *vd*	4509·0	22172	*h*— 766
0	4187·5	23874	*e*— 642	4 *d*	4550·2	21971	*h*— 967
1	4211·5	23738	*d*— 967	0	4563·4	21907	*h*—1031
0	4223·5	23670	*d*—1035	4	4568·4	21884	*h*—1054
1	4226·4	23654	*d*—1051	4	4578·8	21834	*d*—287
0	4236·0	23601	*h* + 663	4 *d*	4587·2	21794	*d*—2911
0	4260·4	23465	*e*—1051	8	4590·8	21777	*d*—2928
1*b*	4264·3	23444	*d*—1261	4 *b*	4598·9	21738	*d*—2967
0	4293·8	23283	*d*—1422	1 *b*	4611·4	21679	*h*—1259
1*b*	4300·0	23249	*d*—1456	0	4631·6	21585	*e*—2931
				0	4639·3	21549	*e*—2967
				2	4646·3	21516	*h*—1422
0	4422·6	22605	*h*— 333	2 *d*	4653·4	21484	*h*—1454

$\Delta\nu$	333	384	509	525	641	667	764	967	1033	1052	1260	1422	1454	2871	2911	2930	2969
	(0)	(0)	(6)	(3)	(8)	(4)	(*o vd*)	(4 *d*)	(0)	(4)	(1 *b*)	(2)	(2 *d*)	(4)	(4 *d*)	(8)	(4 *b*)
ρ	30·0	26·0	19·65	19·05	15·60	14·99	13·09	10·34	9·68	9·53	7·94	7·03	6·88	3·483	3·435	3·413	3·368

The absence of these outer frequencies in certain molecules such as H_2O, CO_2 etc., may be attributed to their feebleness. Certain exceptions may be noted to this general rule, the most conspicuous example being zinc methyl.[5] The Raman spectrum of methyl sulphide is, however, in accordance with the general rule in that the two outermost frequencies attributed to the group $C\diagup\!\!\diagdown\!\!\diagup\!\!\diagdown C$ (S) are weak and diffuse.

One striking feature that comes out from the data collected above is that the principal frequency representing the symmetric oscillation in carbon disulphide is actually multiple. Such a multiplicity is also noted in methyl sulphide and is evidently a necessary accompaniment of the C—S bond.

In view of such an exceptional character of the C—S linkage, the available results are discussed here, in greater detail. Methyl sulphide shows two frequencies, a sharp intense one at 691 accompanied by a feeble and more diffuse line at 746. It is remarkable that the relative intensities and nature of these two lines characteristic of C—S linkage, do not show any change even in widely different classes of compounds containing this linkage although some variations regarding their frequencies are noticeable.

This feature is clearly brought out from the extensive data given below and is, perhaps, one of the strongest arguments to demonstrate that these two Raman lines represent in reality only one oscillation, the principal frequency being represented by the most intense line of the group, and the subsidiary one being in essence a slight modification of the same. This view is further supported by polarisation measurements which show that the two lines are equally polarised.[6]

[5] For a detailed discussion of the Raman spectrum of this compound see Ind. Jour. Phys., Vol. V, p. 145, 1930.

[6] S. Bhagavantam, Ind. Jour. Phys., Vol. V, p. 59, 1930.

Substance			
Methyl mercaptan	C—S	704 (10) s	805 (1 d)
Ethyl ,,	,,	659 (10) ,,	739 (0 d)
Propyl ,,	,,	652 (4) ,,	730 (1 d)
Butyl ,,	,,	656 (5) ,,	707 (0 d)
Isobutyl ,,	,,	670 (3) ,,	770 (1 d)
Isoamyl ,,	,,	659 (5) ,,	741 (2 d)
Phenyl ,,	,,	695 (3) ,,	730 (0 b)
Methyl sulphide	,,	691 (6) ,,	743 (2 d)
Methyl disulphide	,,	695 (6 s) ,,	740 (0 d)
Ethyl sulphide	,,	657 (4) ,,	792 (0 d)
Ethyl disulphide	,,	641 (3) ,,	764 (ovd)
Propyl sulphide	,,	646 (5) ,,	781 (2 d)
Butyl ,,	,,	655 (3) ,,	794 (1 d)
* Isobutyl ,,	,,	723 (3) ,,	
* Allyl sulphide	,,	732 (8) ,,	918 (2 d)
Thiophene	,,	607 (4) ,,	835 (1 b)
Carbon disulphide	C=S	652 (10) ,,	730 (2 b)
Phenyl mustard oil (7)	,,	695 (0)	756 (0)
* Allyl thiocyanate (8)	,,	693 (1)	710 (1)
Ethyl isothiocynate (8)	,,	645 (7)	796 (2)

The CS oscillations are also unique in another respect. It is seen from the above table that not only do they remain unaffected by the nature of the group attached to the carbon atom, but even the changes in the manner of binding between

7. N. N. Pal and P. N. Sen Gupta, Ind. Jour. Phys., Vol. V, p. 13, 1930.
8. A. Dadieu. Wien, Berichte, Band 139, 629, 1930.

* A marked increase in the vibration frequencies of the CS group is noticed in iso-compounds and in compounds having an ethylenic linkage.

TABLE V

Propyl Sulphide.

Intensity.	λ_{Ra} A.U.	ν (Vac).	$\Delta\nu$	Intensity.	λ_{Ra} A.U.	ν (Vac).	$\Delta\nu$.
5	4083·0	24485	*a*—2904	2	4498·0	22226	*h*— 712
5	4088·2	24454	*a*—2935	4	4503·0	22201	*h*— 737
6	4093·5	24422	*a*—2967	3	4512·2	22156	*h*— 782
4	4099·8	24385	*b*—2969	3	4526·3	22087	*h*— 851
3	4104·5	24357	*c*—2933	6	4535·0	22045	*h*— 893
3 *d*	4155·6	24057	*d*— 648	3	4552·4	21960	*g*—1035
0	4160·7	24028	*d*— 677	8	4563·5	21907	*h*—1031
0	4166·5	23994	*d*— 711	0	4568·1	21885	*h*—1053
3	4170·9	23969	*d*— 736	0	4573·0	21861	*h*—1077
2	4179·2	23921	*d*— 781	8	4579·1	21832	*d*—2873
2 *d*	4191·4	23852	*d*— 853	10	4585·5	21802	*d*—2903
2	4198·3	23812	*d*— 893	10	4591·7	21772	*d*—2933
8	4223·0	23673	*d*—1032	8	4598·5	21740	*d*—2965
0	4227·1	23650	*d*—1055	0	4607·2	21699	*g*—1296
2 *d*	4231·7	23625	*d*—1080	3	4618·7	21645	*h*—1293
2	4269·9	23413	*d*—1292	2	4626·0	21610	*h*—1328

1	4277·0		23874		d—1331		2		4639·3		21582		e—2934														
2	4292·7		23289		d—1416		1		4637·2		21559		e—2957														
3 sh	4299·8		23253		d—1452		4		4646·0		21518		h—1420														
0	4366·3		2279·2		h— 146		6 d		4653·8		21482		h—1456														
3	4412·6		22656		h— 282		4		4982·0		20067		h—2871														
1	4431·9		22557		h— 381		5		4992·2		20026		h—2912														
0	4442·3		22505		h— 433		5		4997·2		20006		h—2932														
5	4464·5		22398		h— 646		4		5005·7		19972		h—2966														
2	4491·2		22260		h— 678																						

Δν	146	282	381	433	646	677	712	737	781	852	893	1031	1054	1079	1293	1329	1418	1454	2872	2903	2934	2965					
	(1)	(2)	(1)	(0)	(4)	(2)	(2)	(4)	(3)	(3)	(5)	(8)	(0)	(1)	(3)	(2)	(4)	(6 d)	(8)	(10)	(10)	(8)					
ν	68·5	35·5	26·2	23·1	15·48	14·77	14·04	13·57	12·80	11·74	11·20	9·70	9·49	9·27	7·73	7·53	7·05	6·88	3·482	3·445	3·408	3·373					

the carbon and sulphur atoms do not appear to influence to any great extent the magnitude of these frequencies.

It is interesting to note that the 691 line of methyl sulphide splits up into three more or less equally intense components at 639, 657 and 690 in ethyl sulphide. In propyl and butyl sulphides an even more complicated structure is observed. The Raman line at $\Delta\nu$ 284 of methyl sulphide shows also an exactly similar splitting in the higher members. This line is broad and diffuse in methyl sulphide, and does not show any structure. In ethyl sulphide, on the other hand, it splits up into three distinct well defined lines at 302, 336 and 391 of more or less equal intensity. The further splitting of this line in higher compounds is closely analogous to the 691 frequency. In propyl sulphide we find that each of them splits up into four components, but differences in the relative intensities of the components begin to appear. It is of great interest to note that the ratio of the separation between the three components of the 284 line in ethyl sulphide is of the same order of magnitude as that between the 691 components. Such a closely related behaviour of these two frequencies points to the fact that the above phenomenon has probably the same origin in both cases, the nature of which, however, is not understood at present. This important feature hitherto not known and revealed for the first time by a study of the organic sulphides is peculiar to the C—S group.

Coming to the other organic sulphides we find that in the higher members a number of lines appear in addition to those present in methyl sulphide. These evidently include the C—C oscillations in addition to those due to CS and CH groups. While the C—C oscillations in mercaptans[9] give rise to diffuse bands they are fairly well defined and sharp in the sulphides.

[9] S. Venkateswaran, Ind. Journ. Phys., Vol. 5, p. 219, 1930.

The nature of the CH oscillations in the various hydrocarbons has been discussed in another paper.[10] Interesting differences are noticed regarding the relative intensities of the components of this band in the normal and iso-compounds. In butyl sulphide, for example, we find that the central component $\Delta\nu$ 2914 is the most intense, the outer components being somewhat less intense. On the other hand, the two outer components of this band, *viz.*, $\Delta\nu$2869 and 2966 are the most intense in iso-butyl sulphide, the inner ones being comparatively less intense and more diffuse. This difference in the relative intensities of the components of the CH band in the normal and corresponding iso-compounds appears to be of general nature.

In conformity with the observations in other classes of compounds an increase in the continuous spectrum is noticed in the higher members of the series. In butyl and isobutyl sulphides a few feeble Raman lines were masked owing to the strong continuous background.

The striking feature of the spectrum of allyl sulphide is the presence of a Raman frequency $\Delta\nu$ 1634 which is the most intense and which does not appear with the other organic sulphides. This frequency is evidently connected with the unsaturated bond present in the molecule and is in agreement with the value (1630 to 1655) obtained recently by Lespeau and Bourguel [11] as characteristic of the ethylenic linkage from an extensive study of such compounds. The presence of the extreme components of the C—H band, *viz.*, $\Delta\nu$ 3009 and 3084 in allyl sulphide is also attributable to the presence of ethylenic linkage in the molecule. It may be remarked here that the Raman frequencies of this

[10] S. Venkateswaran and S. Bhagavantam, Ind. Journ. Phys., Vol. V. p. 129, 1930.

[11] M. R. Lespeau and M. Bourguel, Comptes. Rendus, 190, p. 1504, 1930. also Bulletin. Soc. Chimique, 47 p. 1365, 1930.

TABLE VI

Butyl Sulphide.

Intensity.	λ_{Ra} A.U.	ν (Vac).	$\Delta\nu$	Intensity.	λ_{Ra} A.U.	ν (Vac).	$\Delta\nu$
4	4008·3	24485	*a*—2904	3	4529·6	22071	*h*— 867
4	4068·2	24454	*a*—2935	3	4535·0	22045	*h*— 893
3	4094·0	24419	*a*—2970	0	4538·8	22026	*g*— 969
2	4098·1	24395	*b*—2959	1	4550·1	21971	*h*— 967
1	4104·5	24375	*c*—2933	2	4556·0	21943	*h*— 995 }
2	4156·3	24053	*d*— 652				*g*—1052 }
1	4160·7	24028	*d*— 677	4	4568·0	21885	*h*—1053
0	4167·2	23990	*d*— 715	6 *dr*	4579·2	21832	*d*—2873 }
0	4169·4	23978	*d*— 727				*h*—1106 }
0 *d*	4174·0	23951	*d*— 754	8 S	4587·8	21791	*d*—2914
0	4181·0	23911	*d*— 794	5	4592·0	21771	*d*—2934
1	4193·6	23839	*d*— 866	5	4597·5	21745	*d*—2960
1	4198·0	23814	*d*— 891	3	4619·9	21639	*h*—1299
0	4212·0	23735	*d*— 970	3	4625·4	21614	*h*—1324 }
0	4218·5	23698	*d*—1007				*e*—2902 }
3	4227·1	23650	*d*—1055	3	4632·8	21579	*e*—2937

| | | |

TABLE VII

Iso-butyl Sulphide.

Intensity.	λ_{Ra} A.U.	ν(Vac.)	$\Delta\nu$.	Intensity.	λ_{Ra} A.U.	ν (Vac.)	$\Delta\nu$.
3	4082·8	24486	$a-2903$	4	4518·0	22127	$h-811$
3	4088·5	24452	$a-2937$	0	4527·0	22084	$h-854$
5	4094·0	24419	$a-2970$	4d	4547·8	21982	$h-956$
3	4099·0	24389	$b-2965$	0	4555·5	21945	$h-993$
1	4105·5	24351	$c-2939$	0	4572·0	21866	$h-1072$
2	4168·8	23981	$d-724$	8b	4577·8	21838	$d-2867$
2dr	4174·2	23950	$d-755$	3d	4581·5	21821	$h-1117$
3	4184·5	23891	$d-814$	4d	4587·0	21795	$d-2910$
0	4202·0	23791	$e-725$	4d	4592·4	21769	$d-2936$
3b	4209·7	23748	$d-957$	8b	4598·5	21740	$d-2965$
1d	4239·0	23584	$d-1121$	0	4613·0	21672	$g-1323$
2d	4276·6	23376	$d-1329$	3	4626·0	21611	$\left\{\begin{matrix} h-1327 \\ e-2909 \end{matrix}\right\}$
1d	4293·0	23287	$d-1418$	1	4637·5	21557	$e-2959$
3d	4299·5	23252	$d-1453$	0	4646·0	21518	$h-1420$
1	4425·0	22598	$h-345$	5d	4654·0	21481	$h-1457$

1d		4438·5		22594		h − 414		3		4981·8		20067		h − 3871									
1d		4442·0		22506		h − 432		1		4992·3		20036		h − 3912									
3		4500·2		22215		h − 723		3		5005·8		19971		h − 3967									
3		4506·4		22186		h − 754																	
Δν :—	345,	414,	432	723	754	812	854	956	993	1072	1119	1333	1419	1455	2869	2910	2936	2966					
	(1)	(1)	(1d)	(3)	(3)	(4)	(0)	(4d)	(0)	(0)	(3d)	(3)	(0)	(5d)	(8b)	(4d)	(4d)	(8b).					
ρ :—	29·0	24·2	28·1	13·8	13·3	12·3	11·7	10·5	10·07	9·33	8·94	7·53	7·05	6·87	3·486	3·436	3·406	3·372					

substance show a tendency to be arranged as close doublets.[12] The CS oscillations of allyl sulphide assume a distinctly higher value than in the other compounds (see Table XI). This may be ascribable to the presence of the unsaturated linkage in the molecule.

In all the sulphides, the 'wings' accompanying the incident lines which are presumably due to rotational transitions, are somewhat prominent, although data given in page 55 for the depolarisation factor and magnetic birefringence show that they are only feebly anisotropic. This broadening of the incident lines is strikingly noticeable in all organic compounds having the sulphur atom in the molecule.

No compound having two sulphur atoms attached to each other in the molecule has been hitherto investigated. The Raman spectra of methyl and ethyl disulphides are therefore of special interest (see Tables II and IV). In the following table the frequencies of methyl sulphide and disulphide are compared, the figures within the brackets indicating their intensities.

TABLE VIII

Methyl sulphide		284		691	743	1335	1425	2916	2984
		(1d)		(6S)	(2d)	(1)	(1d)	(8)	(4d)
Methyl disulphide	243	284	512	695	740	1337	1425	2914	2987
	(1d)	(0d)	(6S)	(6S)	(0d)	(0)	(0d)	(6)	(3d)

The appearance of a new prominent line at $\Delta\nu$ 512 in methyl disulphide which is not present in the corresponding sulphide should be noted. This line is absent in ethyl

[12] Similar results were obtained in the case of allyl alcohol ; see A. S. Genesan and S. Venkateswaran, Ind. Journ. Phys., Vol. IV, p. 195, 1929. See also S. Venkateswaran and A. Karl, Zeits. Phy. Chem., p. 466, 1928.

sulphide, but appears with prominence in ethyl disulphide. The results unmistakably suggest that it is connected with the S—S bond present in the two disulphides. The value 512 is, however, appreciably less than the frequency of vibration S_2 as obtained by fluorescence and absorption of sulphur vapour, *viz.*, $\nu=724{\cdot}5$. This difference indicates that the sulphur atoms in the S_2 molecules are more firmly bound than in the disulphide. Such differences are noticed in various other cases, *e.g.*, C—O, C=O and C—C, C=C, C≡C,* and are attributed to a difference in the nature of the chemical bonds. On the view that the atoms in S_2 are attached with a double bond (S=S), the sulphur atoms in the latter group are presumably attached with a single bond (C—S—S—C). The possibility that the two sulphur atoms in S_2 molecule may be bound by tetravalent bonds must also be mentioned here. This indicates a trivalent bond between the sulphur atoms in the disulphides. The relatively low (S—S) oscillation frequencies obtained for both S_2 and disulphides, *viz.*, 724 and 512 do not, however, favour such a view. The above result is of great significance and clearly indicates how a study of the Raman spectra affords a convenient and powerful method of investigating problems connected with the constitution of organic compounds.

The splitting of the C—S oscillation frequency as we pass from the methyl to ethyl and higher members noticed in the foregoing sections appears also to be characteristic of the S—S oscillation in the group of disulphides. The frequency 512 in methyl disulphide splits as we pass to ethyl disulphides into two frequencies at 509 and 525.

* C—O :— $\Delta\nu$ 1040 (approx.)
C=O :— $\Delta\nu$ 1700 ,,
C—C :— $\Delta\nu$ 900 ,,
C=C :— $\Delta\nu$ 1630 ,,
C≡C :— $\Delta\nu$ 2120 ,, (M. M. Bourguel and P. Daure, Soc. Chimique, 4th series 47, p. 1349, 1930).

TABLE VIII.

Allyl Sulphide.

Intensity.	λ_{Ra} A.U.	ν (Vac.)	$\Delta\nu$.	Intensity.	λ_{Ra} A.U.	ν (Vac.)	$\Delta\nu$.
2	4086·7	24463	$a-2926$	8S	4502·4	22204	$h-734$
3	4090·3	24441	$a-2948$	8S	4506·4	22184	$h-754$
2	4095·2	24412	$a-2977$	2d	4539·8	22021	$h-917$
			$b-2942$	0d	4556·6	21940	$h-998$
4	4100·8	24379	$b-2975$	0d	4565·4	21898	$h-1040$
			$a-3010$	0d	4572·9	21862	$h-1076$
3d	4112·5	24309	$a-3080$	8	4587·7	21791	$d-2914$
3d	4115·0	24294	$d-411$	3	4593·8	21762	$d-2943$
0	4126·0	24230	$a-3159$	0d	4598·5	21740	$h-1198$
4dr	4143·8	24126	$d-579$	5	4601·3	21727	$d-2978$
6	4169·9	23975	$d-730$	8	4607·8	21696	$d-3009$
6	4173·6	23953	$d-752$				$h-1249$
2d	4203·0	23786	$d-919$	6	4618·9	21644	$h-1294$
			$e-730$	4	4623·8	21621	$d-3084$
2d	4253·6	23503	$d-1202$	6	4642·7	21533	$h-1405$
2d	4260·0	23468	$d-1237$	4	4648·3	21507	$h-1431$

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An examination of Table VIII shows that there is a small but definite difference in the values of the CS oscillations in the two compounds. In methyl sulphide its value is $\Delta\nu 691$ whereas in the disulphide it is distinctly higher by four wave numbers. In both cases the line is remarkably sharp and intense.

The author desires to thank Prof. Sir C. V. Raman, F.R.S., for his kind interest in the work.